PATENT SPECIFICATION

(11) 1294723

1294723

DRAWINGS ATTACHED

(21) Application No. 7691/70 (22) Filed 18 Feb. 1970

(31) Convention Application No. 14574 (32) Filed 28 Feb. 1969 in

(33) Japan (JA)

(45) Complete Specification published 1 Nov. 1972

(51) International Classification D01F 7/04

(52) Index at acceptance

B5B 200 35Y 360 38Y 401 436 510 714 720 725 726 728 72Y

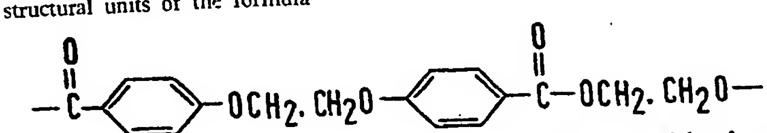
(54) CONJUGATE FIBRES

(71) We, ASAHI KASEI KOGYO KABUSHIKI KAISHA, of No. 25—1, 1-chome, Dojimahamadori, Kitaku, Osaka, Japan, a Body corporate of Japan, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to conjugate fibres. More particularly the invention relates to conjugate filaments or conjugate staple fibres capable of forming spiral crimps and comprising two components, namely polyethylene-1,2-diphenoxyethane-4,4′-dicarboxylate and polyethylene terephthalate.

Two component conjugate filaments obtained by eccentric conjugate spinning of two or more synthetic polymer components having different shrinkabilities are well known. For example, in United States Patent No. 2,931,091 the conjugate spinning of two polycondensate components having different shrinkages in sheathcore or side-by-side relationship is described. Such filaments, when under shrinking conditions in the substantial absence of tension, form spiral crimps and the number of crimps per unit length has a direct relationship with the difference in shrinkages between two components. Such crimps are useful because they give the fibres and materials formed therefrom, bulkiness and elasticity. However, such two component fibres have a decreased ability to form crimps against restraining loads (as can be seen in woven fabrics) and when heat-set their crimpability is markedly reduced and their apparent total shrinkage is decreased. In our Patent No. 1,200,134 we have described and claimed two component conjugate filaments, one component of which is a polyethylene terephthalate polymer and the other component is composed of polyethylene diphenoxyethane-4,4′-dicarboxylate.

The conjugate fibres of the present invention comprise two components, one of which (hereinafter referred to as PEP) contains polyethylene-1,2-diphenoxyethane-4,4′-dicarboxylate as its major component and the other (hereinafter referred to as PET) contains, as major component, polyethylene terephthalate; the shrinkage of the PEP component when treated with boiling being kept to less than 8% of that of the non-treated stretched fibres, if necessary substantially zero; the PET component is made to shrink to a greater extent than the PEP component under crimp-developing conditions and the PET component is arranged so as to occupy the inside of the spiral curls in the crimped state. The fibre possesses a maximum thermal stress of more than 50 mg/d if the requirements $\Delta n_{PEP} > 0.16$ and $\Delta n_{PET} < \Delta n_{PEP} - 0.2$ are satisfied wherein Δn_{PEP} and Δn_{PET} are the birefringences of the PEP and the PET respectively. The term "polyethylene-1,2-diphenoxyethane-4,4′-dicarboxylate (PEP)" as used herein is intended to refer to a polymer component containing 75% by weight or more of repeating structural units of the formula



Thus the PEP may be a copolyester containing up to 25% by weight of a glycol other than ethylene glycol e.g. diethylene glycol, tetramethylene glycol or hexamethylene glycol. The polymer may also be a copolyester containing up to 25% by weight of a dicarboxylic acid other than 1,2-bis(*p*-carboxyphenoxy) ethane e.g. hexahydro-

spun by passing them through a conjugate spinneret and are then wound up. There are many spinnerets known for conjugate spinning. Examples of typical sheath-core type or side-by-side type spinnerets are shown in Figures *6a* and *5a*. In the apparatus shown in Figure *5a*, two polymers A and B are distributed to each spinning hole after passing through respective spinning plates 1 and 2 and are thereafter joined and conjugated at a spinning plate 3 to produce conjugate fibres having the cross-section shown in Figure *5b*. Figure *6a* shows a sheath-core type spinneret. Polymers A and B are joined and conjugated at a spinning plate 3 in a side-by-side relationship and further conjugated as if enclosed by polymer A at a spinning plate 4 to produce sheath-core type conjugate fibres as shown in Figure *6b*. Various kinds of spinning holes having modified or different types of cross-section can be used besides those illustrated above.

In the spinning of the conjugate fibres of the present invention the PET is suitably used in an amount of from 30 to 95%, preferably from 40 to 80% based upon the total conjugate fibre.

The wound-up unstretched filaments obtained from the spinnerets are stretched in known manner using a hot plate or a hot pin and a heating medium such as steam or hot water. Figure 1 shows preferred limits within which the stretching ratio and the stretching temperature may vary in the production of a 1 : 1 polyethylene terephthalate: polyethylene-1,2-bisphenoxyethane-4,4'-dicarboxylate fibre and from it can be seen that a range of less than 3.5 times at 60°C, less than 4 times at 80°C less than 4.5 times at 100°C, and less than 5 times at 120°C, etc. are preferable because the boiling water shrinkage of the PEP is kept low in these ranges. However, it is to be noted that Figure 1 is only one Example and the method of the present invention is not limited thereto.

Further, in order that the birefringences of the two components may satisfy the conditions $\Delta n_{PEP}>0.16$, and $\Delta n_{PET}<\Delta n_{PEP}-0.02$, it is necessary to stretch more than 2.5 times at 60°C, more than 2 times at 80°C and more than 1.5 times at 100°C. The birefringence of each component of the conjugate fibres was measured by a retardation method on the conjugate fibres cut obliquely in a wedge shape at a fixed angle (Journal of Applied Physics, *17* 996, 1966). It is also possible to measure birefringences by Becke's method.

In contrast to the conventional spinning and stretching of PEP or PET alone in which the range of suitable conditions is relatively narrow and the conditions for good spinning and stretching have to be strictly and closely regulated in order to produce uniform fibres, the spinning and stretching conditions for the conjugate fibres of the present invention can be considerably widened.

For example, in Japanese Patent Publication No. 21, 815/1961, it is indicated that a suitable temperature range for stretching PET filaments is from 80°C to 125°C and that stretching above 125°C is difficult (see Figure 1). On the other hand, in British Specification No. 1,046,069, it is stated that PEP filaments are stretched from 1.25 to 2.5 times, and in British Specification 1,047,978, two stage stretching is described. Thus it can be seen that both components of the conjugate fibres of the invention have narrow spinning and stretching conditions. However, when the two components are conjugate spun, far wider stretching conditions are possible and thus the generally preferred higher stretching is obtainable.

The relationship between stretching ratio and boiling water shrinkage of a PEP component at the time of stretching at various temperatures using non-stretched filaments of side-by-side type conjugate fibres obtained by spinning PET (reduced viscosity of 0.19) and PEP (reduced viscosity of 0.75) is shown in Figure 2. As will be seen, it is desirable to employ a relatively high temperature, especially a temperature above 80°C, preferably above 90°C, in order to reduce the shrinkage of PEP component to below 8% in the case of non-heat-treated stretched filaments subjected to heat treatment. The present conjugate fibres may be readily stretched at temperaures above 125°C, which is surprisingly high above the previously proposed stretching temperatures for producing conjugate fibres having good crimps. The shrinkages of the PEP component of the conjugate fibres were measured from the difference between the lengths of the fibres under a load of 500 mg/d, before and after the treatment at 100°C for one hour under no load.

It is necessary, in the conjugate fibres of the present invention that the relations $\Delta n_{PEP}>0.16$ and $\Delta n_{PET}<(\Delta PEP-0.2)$ be satisfied and that the PET component should shrink more than the PEP component under the crimp developing conditions and the PET component be situated in the inside of the curves in the crimped fibres (Figures *7a*—*7c*). Conjugate fibres satisfying these requirements retain the high Young's modulus and high recovery properties of the PET.

Example 1

A PEP having a reduced viscosity of 0.75 and a PET having a reduced viscosity of 0.80 neither component containing any co-polymers were conjugate spun in side-by-side relationship in a conjugate ratio of 1: 1. The molten filaments were cooled by cooling air blown from the side as in the conventional process. The spinneret had 10 spinning holes of 0.3 mm diameter and the spinning temperature, the temperature of cooling air and the take up speed were 280°C, 20°C and 500 m/min., respectively. The resultant unstretched filaments were stretched at 140°C to 4 times their original length to give conjugate fibres of 30d/10 filaments and having Δn_{PEP} of 0.215, Δn_{PET} of 0.175, and a maximum thermal stress of 225 mg/d. The PEP and PET components had boiling water shrinkages of 4% and 9.2% respectively. The fibres had a tenacity of 4.5 g/d, an elongation of 15%, and a 3%-instant-elongation-recovery of 95%. When heat-treated at 160°C for 30 minutes under a load of 3 mg/d, the fibres developed good crimps having a crimping grade of 15%, a crimp number of 22 per inch and a crimp elasticity of 89%. In these fibres the PET component occupied the inside of the curves in the crimps, giving the fibres a stiff handle. The quality of plain woven fabrics woven before heat treatment of the stretched yarn, and then subjected to finishing processing was good.

By way of comparison, when the unstretched spun yarns as described above, were stretched by two times at 70°C (case 1) and three times at 40°C (case 2), the resultant conjugate fibres had Δn_{PEP} of 0.14 and Δn_{PET} of 0.10 (case 1) and Δn_{PEP} of 0.175 and Δn_{PET} of 0.16 (case 2), and a thermal stress of 42 mg/d (case 1) and 45 mg/d (case 2). When subjected to crimp-developing treatment under a load of 3 mg/d, at 160°C for 30 minutes, the crimp developing property as reduced and a crimping degree of less than 5% was obtained in both cases (1) and (2).

Example 2

A PET containing polyethylene terephthalate only and having a reduced viscosity of 0.81 and a PEP having a reduced viscosity of 0.85 and containing 8 mol % of copolymerized succinic acid were conjugate spun using the sheath-core type spinneret shown in Figure 6a. The spinneret had 10 holes of 0.3 mm diameter, the take up speed was 900m/min and the conjugate ratio of PEP to PET was 1: 1. Unstretched fibres having this component as core, were obtained. The unstretched fibres were stretched to 3.5 times their original length in a first stretching step at 130°C and then by 10% in the second continuous stretching step at 130°C to give good conjugate fibres having a maximum thermal stress of 550 mg/d. The PEP and PET components had boiling water shrinkage of 6.5% and 9.5% respectively. These fibres of 25d/10 filaments had Δn_{PEP} of 0.207 and Δn_{PEP} of 0.171 a tenacity of 5.1 g/d, an elongation of 9.2%, a Young's modulus of 112 g/d and an elongation recovery after 3% strain, in terms of the instant recovering property, of 96% and, in terms of the delayed recovering property, of 100%.

The fibres were heat-treated at 160°C for 30 min. to give conjugate fibres in which the PET core component was situated on the inside of the spirals. The crimping grades measured, varying the load imparted upon the conjugate fibres during heat-treatment, are shown in Table 2. As apparent from the table, the crimping grade varies according to the tension during heat-treatment.

TABLE 2

load (mg/d) during heat-treatment at 160°C	0	0.5	1	3	10
crimping grade (%)	420	52	31	21	4

Comparative Example

A PEP having a reduced viscosity of 0.75 and containing 5 mol % of copolymerized polyethylene glycol (molecular weight 1,000) and a PET having a reduced viscosity of 0.8 were conjugate spun as described in Example 1 to give unstretched fibres which were stretched by 4.5 times at 140°C. The PEP component had a boiling water shrinkage of 12% and crimped fibres obtained by heat-treating at 160°C for 30 minutes had the PET component on the outside of the spirals and had a Δn_{PEP} of 0.197, a Δn_{PET} of 0.161 and a maximal thermal stress of 150 mg/d. The fibres had a tenacity of 4.2 g/d, an elongation of 25%, instant and delayed recovering properties after 3% elongation of 71% and 91%, respectively, a Young's modulus of 42 g/d and there was no feeling of stiffness in the handle of the fibres. The crimping characteristics of the crimped fibres were crimping grade 52% number of crimps 6.3 cm., and crimp elasticity 65%.

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1294723 COMPLETE SPECIFICATION

3 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

FIG. 1

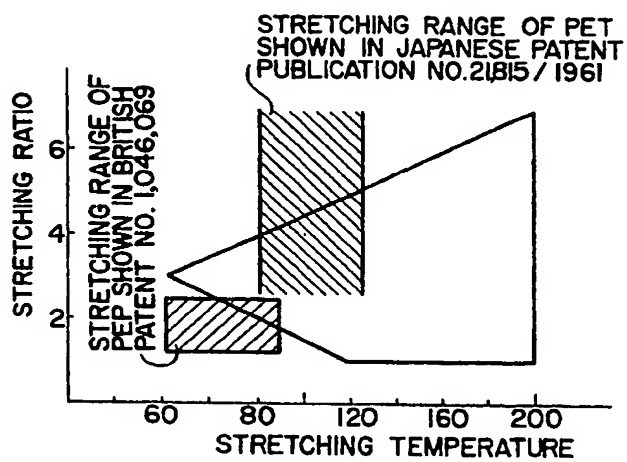


FIG. 2

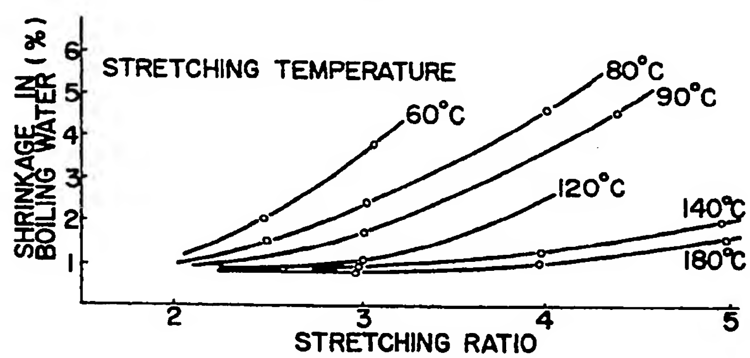


FIG. 5a

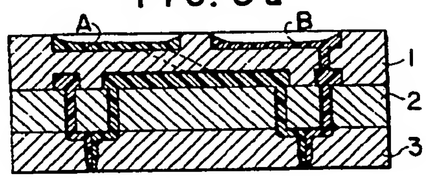


FIG. 5b

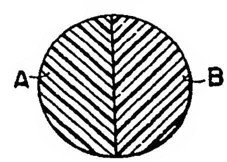


FIG. 6a

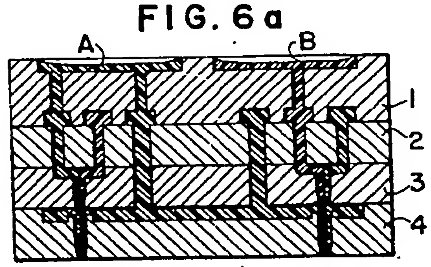


FIG. 6b

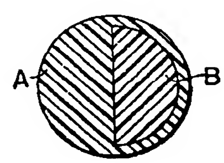


FIG. 7a

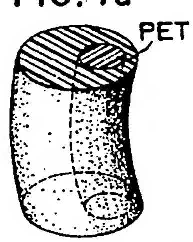


FIG. 7b

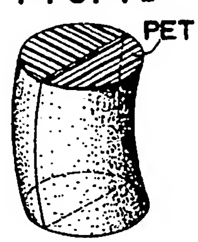


FIG. 7c

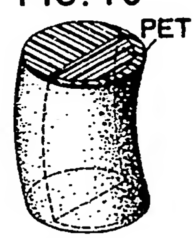
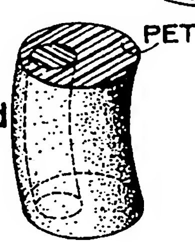


FIG. 7d



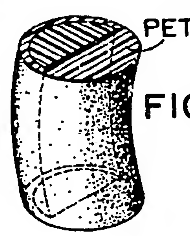


FIG. 7e